A Post–Cure Study of Glass/Vinyl Ester Laminates Fabricated by Vacuum Assisted Resin Transfer Molding

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Technical Report

A Post–Cure Study of Glass/Vinyl Ester Laminates Fabricated by Vacuum Assisted Resin Transfer Molding

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ABSTRACT

A post-cure study was made of a vinyl ester laminate fabricated by vacuum assisted resin transfer molding. One day after fabrication the glass transition temperature (Tg) was about 154 F and the flexural strength was 52 ksi, which are low values. With time at room temperature, however, both strength and Tg increased to acceptable levels. Room temperature post-curing increased the Tg to about 200 F and the flexural strength to 78 ksi. In addition it was found that the resin cures very rapidly at elevated temperature, which allows the resin Tg to remain above the temperature of the environment for most heating rates. Based on increases in strength and Tg due to post-curing reactions at ambient temperature and the rapid increase in Tg with the temperature of the environment, we concluded that post-curing of structures fabricated by VARTM is not necessary.

ADMINISTRATIVE INFORMATION

The work described herein was conducted under the Organic Composites Ship Structures Project (RH21S12) as part of a Congressional Special Interest Initiative, Navy Program Element 0621221N. The project was sponsored and managed by the Office of Naval Research, ONR 334, and executed by the Carderock Division, Naval Surface Warfare Center under work unit 1-6600-042-40.

INTRODUCTION

Laminating resins used in marine construction are as a rule not fully cured. Although these materials are called "room temperature curing" or "cold curing" resins, the reaction exotherm increases the temperature well above ambient, which advances the cure state. Information on the role of resin exotherm on the degree of cure is not available. The purpose of this study was to determine if composite structures for Naval applications should be post-cured, particularly those made by vacuum assisted resin transfer molding (VARTM), which are characterized by low resin contents and therefore low exotherm temperatures.

The degree of cure cannot be directly measured, but it can be indirectly assessed using differential scanning calorimetry (DSC). During a DSC scan, any initially uncured component cures during the test, and the DSC detects the heat of reaction of this uncured component. To determine the percent cure of a given sample, the heat of reaction (per unit weight) of the specimen is assumed to be proportional to the fraction of uncured resin. That is, the percent cure of a specimen = $(1-\Delta H_x/\Delta H_c) \times 100$, where ΔH_x is the heat of reaction of the specimen and ΔH_c is the heat of reaction measured during full cure. This method works well for neat resin samples, but its usefulness for laminates depends on the accuracy of measuring the resin content of each specimen tested. This is difficult given that a DSC uses roughly

10 mg samples.

The degree of cure is related to the crosslink density. There is a maximum possible crosslink density that a given thermoset resin could achieve given enough time at temperature, and as mentioned, the typical resin in marine laminates operates at less than 100 percent reacted (1). There are many resin properties which depend on the crosslink density, so there are many indirect methods which can be used to assess the degree of cure once the methods are calibrated with data established by DSC measurements.

In a study at Dow Chemical Co. (2), Barcol hardness, acetone weight gain, residual styrene content, heat distortion temperature (HDT), and glass transition temperature measured with Dynamic Mechanical Analysis (DMA) were all compared with DSC data. All five methods were acceptable alternatives to DSC, with the exception of Barcol hardness, which was insensitive to degree of cure above 85%. The Dow study reported that the glass transition temperature (Tg) of the vinyl ester evaluated (Derakane 411-45) increased substantially with degree of cure. The data show that neat resin castings were 73.5 % cured after 1 day at room temperature and had a Tg of only 112 °F. Tg was a essentially proportional to the degree of cure, eventually reaching about 225 °F at 100 % cure.

In our study, flexural strength and glass transition temperature were used to characterize the VARTM laminate. The laminate was composed of 6 plys of 24 oz woven roving (OC24P-107B) and a brominated vinyl ester (Dow Derakane 510A). It was cured with 1.25% MEKP and 0.3% CoNap. The weight percent glass was measured at 71.3 and the void content was negligible.

EVALUATION PROCEDURE

The flexural strength and DMA scans of a laminate made by VARTM were measured as a function of time at room temperature, and also after various post-cure conditions.

The flexural testing was done in the warp direction using ASTM D790 (3-point bend) at a span-to-depth ratio of about 32:1. The thermal analysis was done using a Polymer Labs MK II DMTA (Dynamic Mechanical Thermal Analysis) in the single cantilever beam mode at 10 Hz. The data was taken at heating rates of 5 F/min (3 C/min) and 18 F/min (10 C/min).

FLEXURAL STRENGTH RESULTS

The flexural strength as a function of post-cure conditions is given in Table 1, and plotted in Figure 1. The raw data is provided in the Appendix. It is clear from inspection of the flexural strength data that the resin continued to cure slowly for many months while held at ambient temperature. This room temperature post-cure allowed the laminate to develop a flexural strength comparable to that attained with at 140 F post-cure.

It appears from this data that an optimum post-cure temperature exists, which for this resin is about 160 F. The post-cures at 180 F and 200 F resulted in a 20% decrease in strength. Since these temperatures are well below those required for resin degradation, the most likely cause for the strength loss is a decrease in resin failure strain to below the 4% minimum value required for full laminate mechanical property development (3).

Table 1. Flexural strength as a function of post-cure conditions.

Strength (ksi)	Post-Cure Temperature; Time
52.1	Ambient; 24 hours
63.8	Ambient; 1 week
73.1	Ambient; 1 month
70.2	Ambient; 3 months
77.8	Ambient; 6 months
78.4	140 F; 8 hours
89.8	160 F; 4 hours
69.6	180 F; 4 hours
72.1	200 F; 4 hours

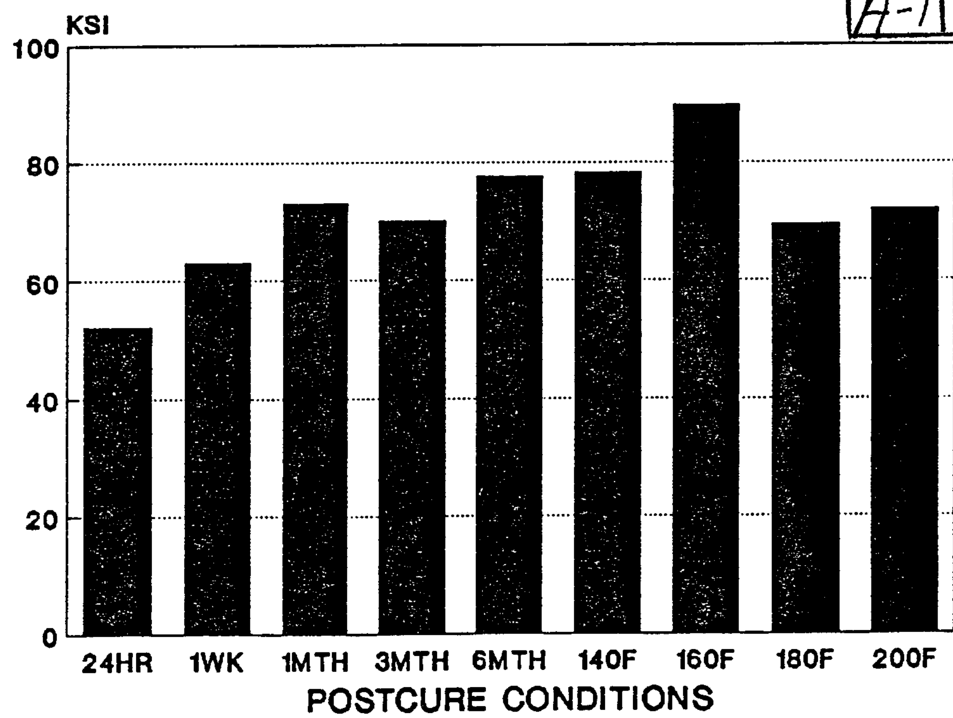

Figure 1. Flexural strength of WR/510A as a function of post-cure conditions.

THERMAL ANALYSIS RESULTS

The DMA scans taken in this study are given in Figures 2-10. Figure 2 shows the modulus (log E') as a function of laminate temperature after 24 hours at room temperature, Figure 3 after 1 week, Figure 4 after 1 month, Figure 5 after 3 months, and Figure 6 after 1 year. Figure 7 is the modulus-temperature plot for the sample post-cured at 140 °F, Figure 8 is the behavior after a 160 °F post-cure, Figure 9 after 180 °F, and Figure 10 after a 200 °F post-cure.

Figures 2-5 were taken at a heating rate of 5 °F/min (3 °C/min). We learned in this study that this heating rate is too slow. It gives the material enough time at temperature to post-cure during the test, and the DMTA then measures the Tg of the post-cured material. Although it appears from the data that the resin Tg is 250 °F (120 °C) in Figures 2-5, this is the post-cured value.

Inspection of Figures 2-5 show a transition, indicated by a drop in modulus, at temperatures well below 250 °F. For example, in Figure 2 the transition starts about 154 °F (68 °C). We believe that this transition is the actual Tg of the material.

Figures 6-10 show the DMA data measured with a heating rate of 18 °F/min (10 °C/min). Interpretation of the data is straightforward because the material cannot cure fast enough at this rate to keep its Tg above the test temperature. The value of Tg is taken at the knee in the modulus-temperature plots. The knee is located by the intersection of lines extrapolated from linear portions of the curve, as shown on each plot.

We have determined the value of Tg from the DMA plots and plotted these values in Figure 11. For comparison we show the DMA data taken in the Dow study in Figure 12.

The most significant discovery is that the Tg increases almost 50 °F after a year at room temperature. As mentioned, flexural strength also increases with room temperature post-curing. The data in Figure 11 supports and provides an explanation for the mechanical property data.

It is interesting to compare the data taken by Dow on Derakane 411 with that generated in this study on Derakane 510A. In both cases, the difference between newly fabricated Tg and maximum Tg was about 100 °F. Also, the initial increase in the degree of cure did not improve the Tg in either study.

DISCUSSION

The data taken in this study indicate that post-cure requirements should not, in general, be imposed upon laminates for use in Naval structures, including those made with VARTM. Three facts have allowed us to make this statement: 1) the laminate strength increases to an acceptable value with time at ambient conditions, 2) the resin Tg increases to an acceptable value with time at ambient conditions, and 3) the resin Tg increases rapidly with the temperature of the environment.

The main concern with the cure state of resins is the low Tg associated with low crosslink densities. Although the cure state can advance rapidly at elevated temperature, failure could result from a temperature rise too rapid for the material to respond. Our data indicates that this rate of temperature increase is between about 5 °F/min and 20 °F/min for Derakane 510A, that is, at rates below 5 °F/min the post-curing reactions will keep the Tg above the temperature of the environment, but heating rates higher than 20 °F/min could allow the temperature to exceed Tg. We feel that post-cure requirements should be imposed only if rapid rates of temperature increase are expected.

SUMMARY

A vinyl ester laminate fabricated by VARTM was evaluated to determine if these low resin content materials should be post-cured due to a reduction in resin exotherm. Given the results listed below, we concluded that post-curing is not necessary unless a rapid temperature increase is expected soon after fabrication.

1. The mechanical and thermal properties of the laminate were initially relatively low due to low percent cure.

2. Room temperature post-cure increased the flexural strength from its initial value of 52 ksi to 78 ksi after 6 months in ambient conditions, a value comparable to that attained with a 140 °F post-cure.

3. Room temperature post-cure increased the Tg from its initial value of 154 °F to about 200 °F after a year in ambient conditions.

4. The degree of cure increased rapidly with temperature. When heated at 5 °F/min the resin Tg remained above the temperature of the environment. However, when heated at 18 °F/min the temperature exceeded Tg.

5. The optimum post-cure temperature for Derakane 510A is 160 °F. Higher temperature post-cures result in a loss in strength, probably due to a reduction in resin failure strain.

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3. T. Juska, J.S. Mayes, and M.J. Russell, "Evaluation of Marine Construction Materials and Fabrication Methods", Proceedings of MACM-5, Composites Education Association, Inc., Melbourne, FL, April 18-20, 1994.

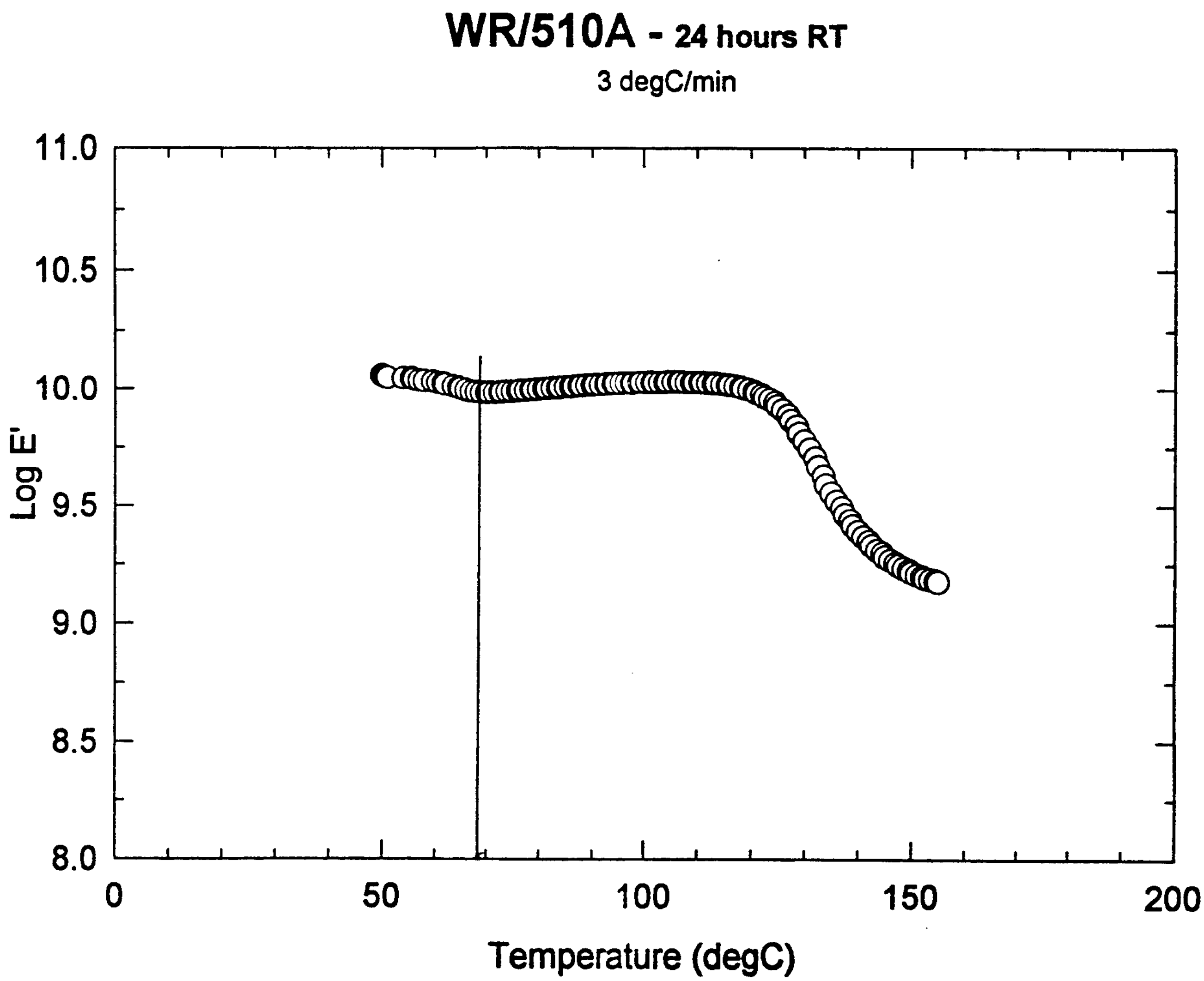

Figure 2. Modulus-temperature behavior of WR/510A 24 hours after fabrication.

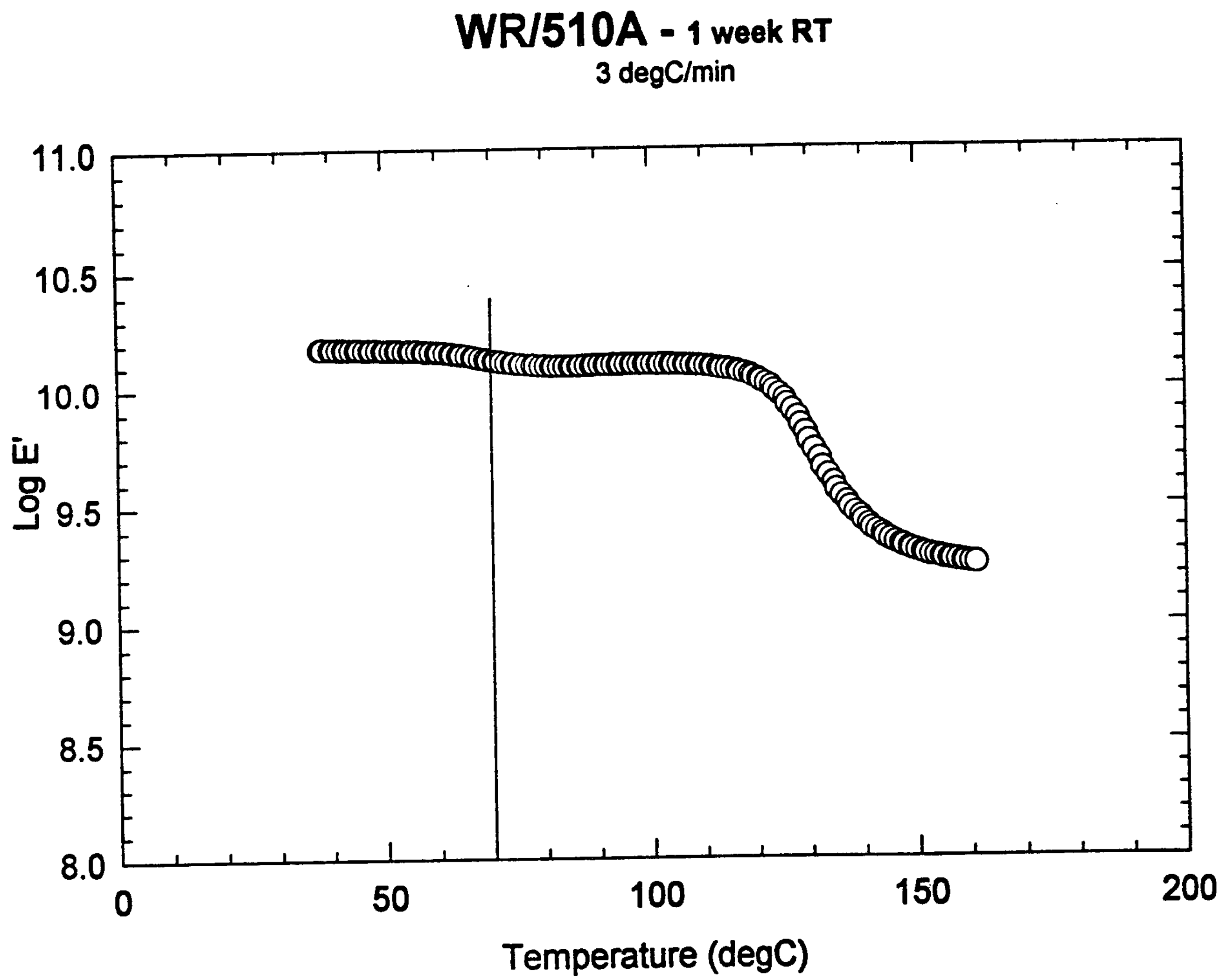

Figure 3. Modulus-temperature behavior of WR/510A 1 week after fabrication.

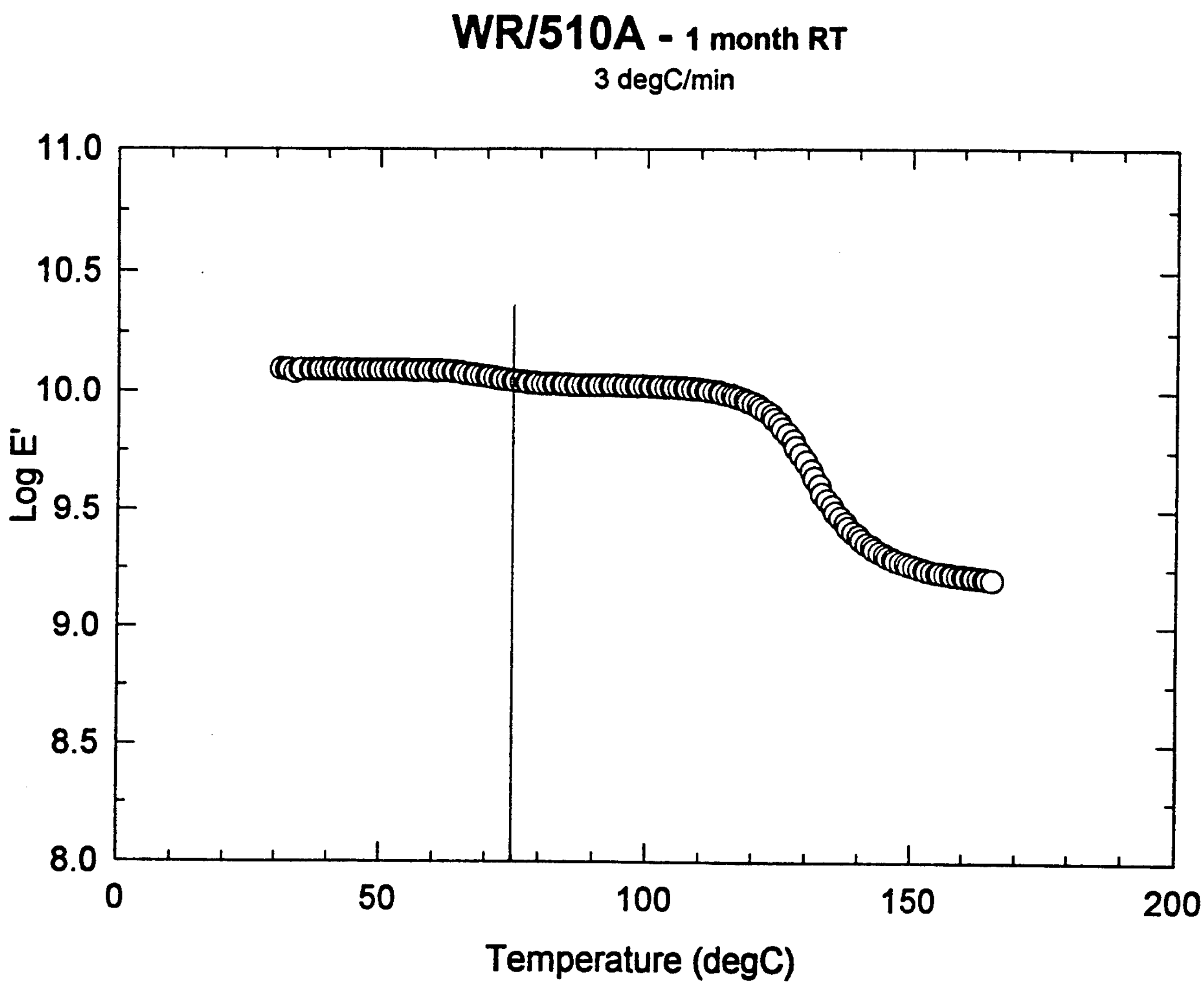

Figure 4. Modulus-temperature behavior of WR/510A 1 month after fabrication.

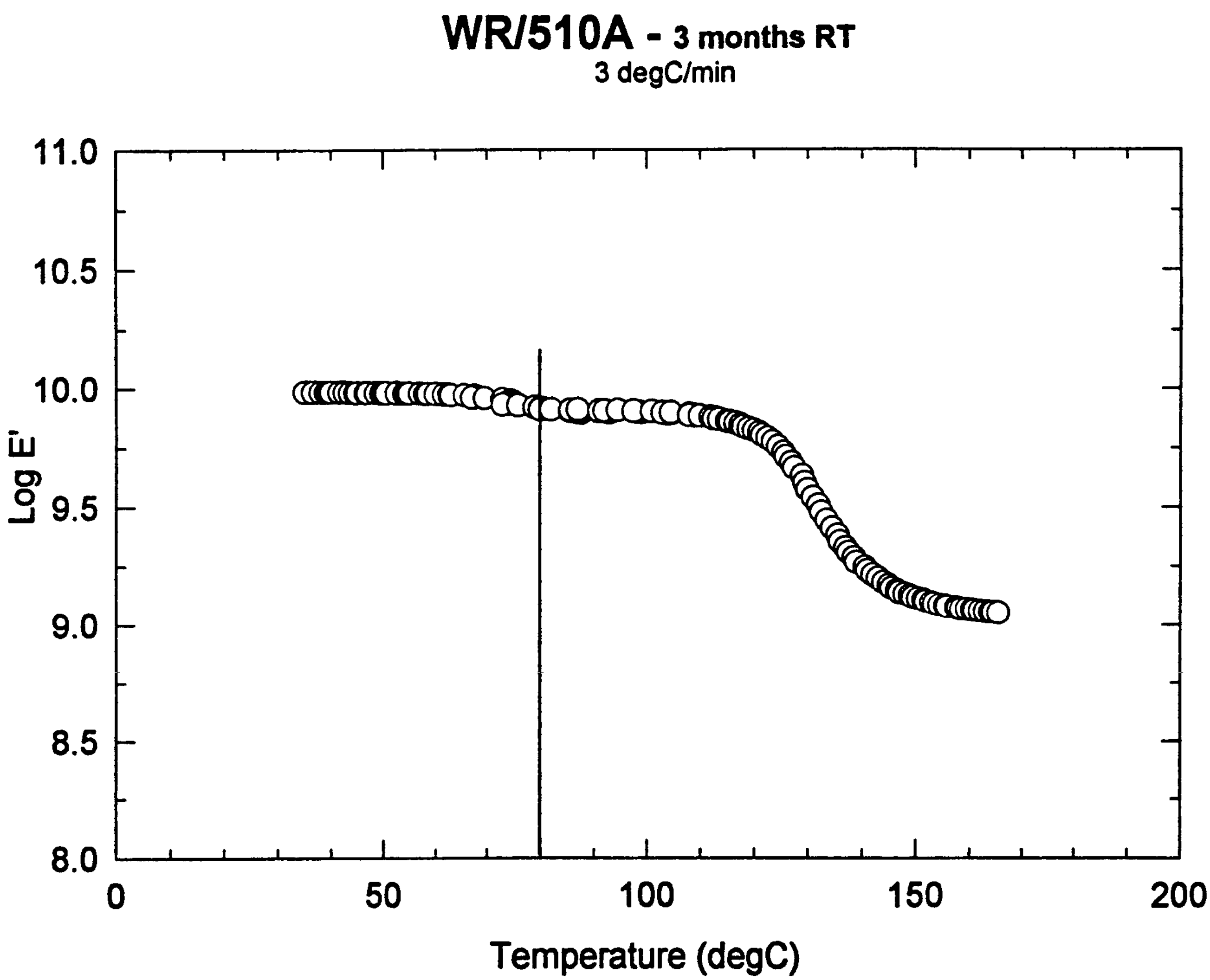

Figure 5. Modulus-temperature behavior of WR/510A 3 months after fabrication.

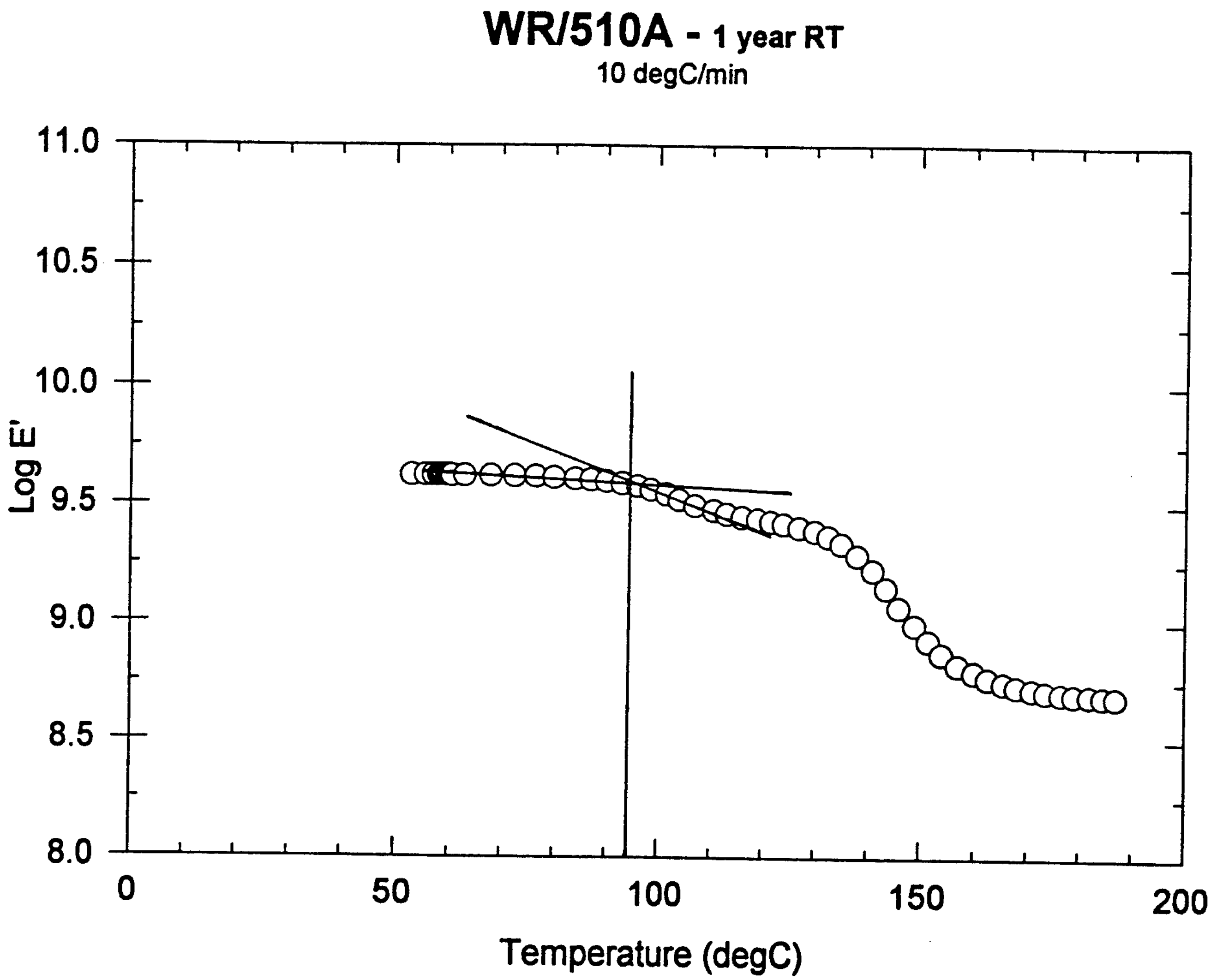

Figure 6. Modulus-temperature behavior of WR/510A 1 year after fabrication.

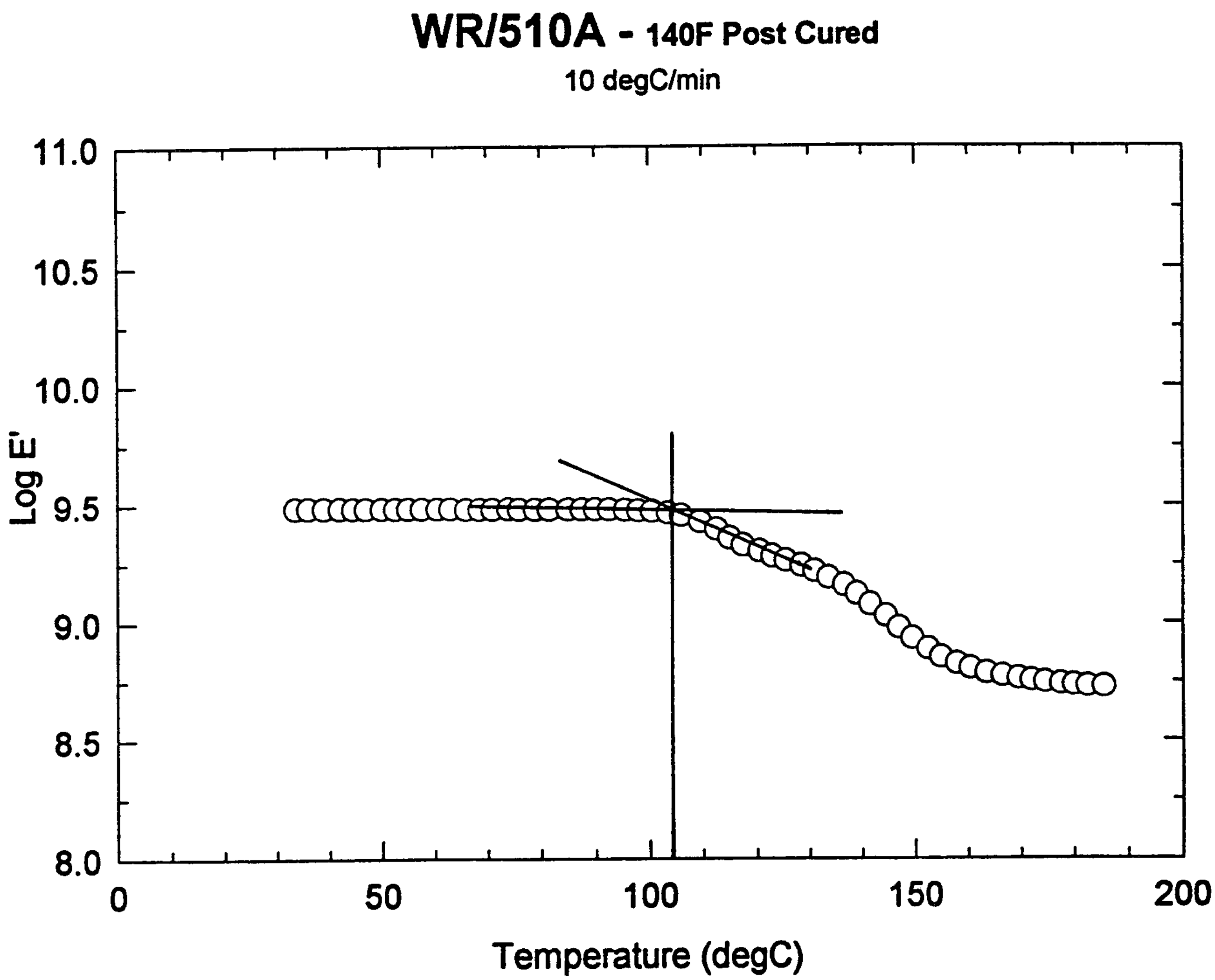

Figure 7. Modulus-temperature behavior of WR/510A after a 140 F post-cure.

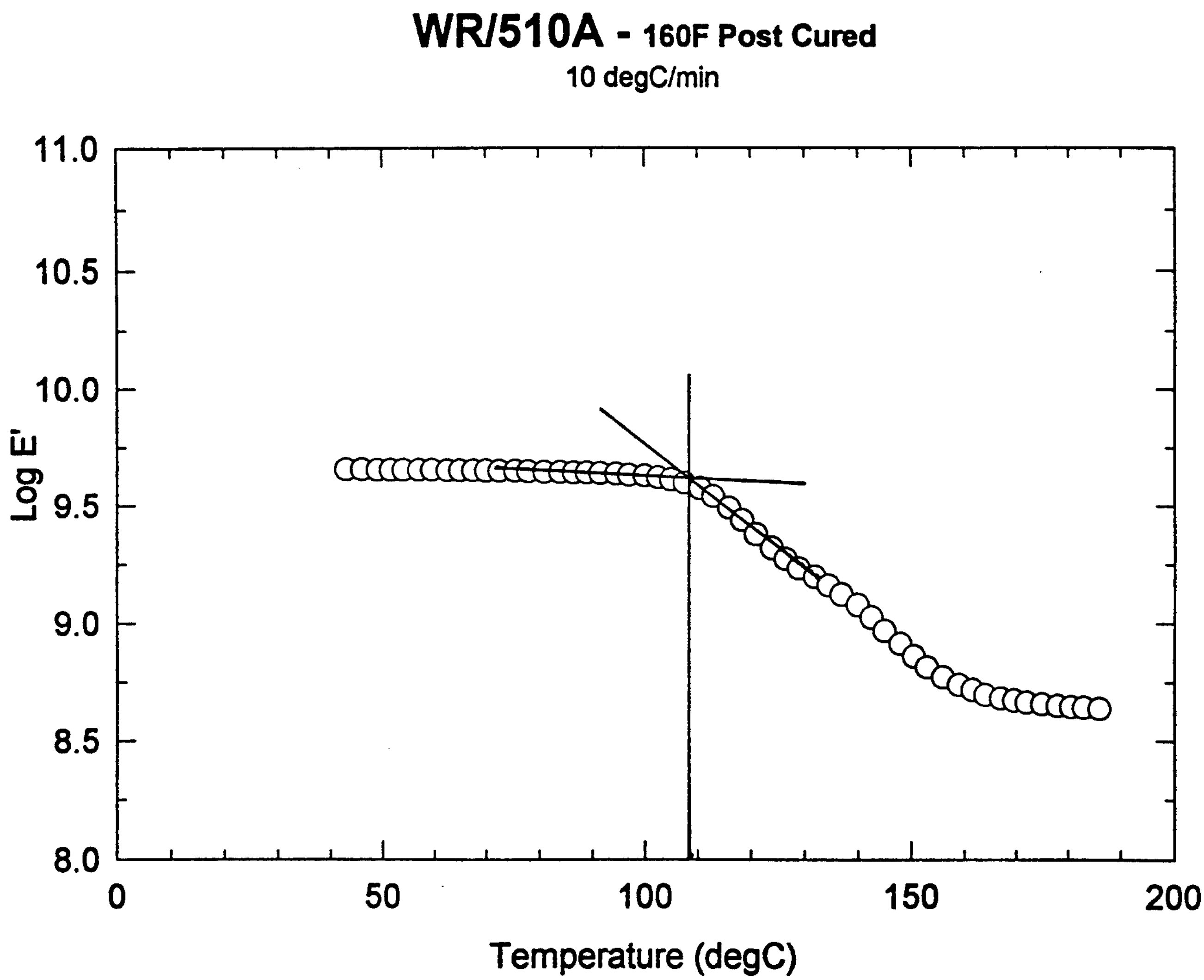

Figure 8. Modulus-temperature behavior of WR/510A after a 160 F post-cure.

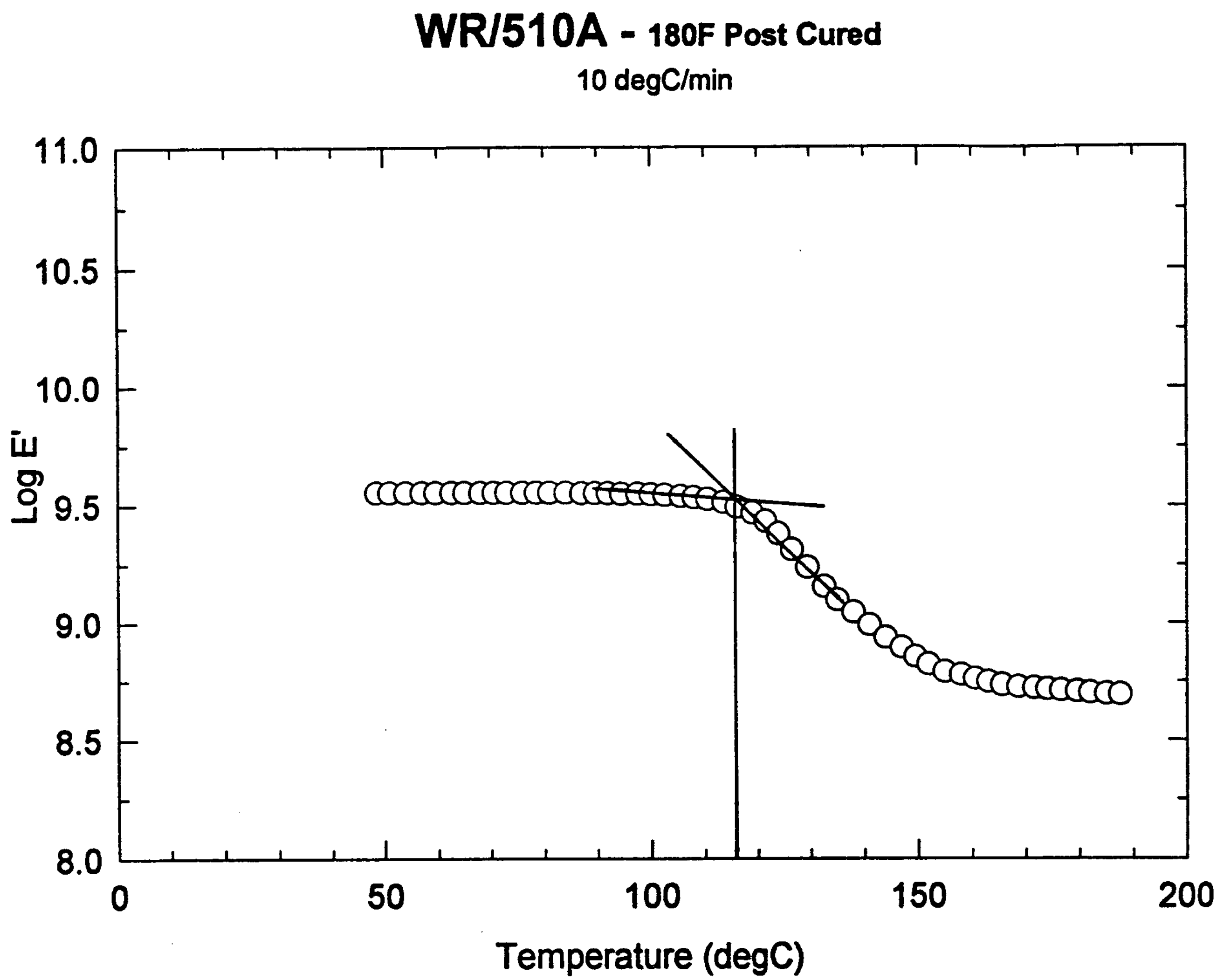

Figure 9. Modulus-temperature behavior of WR/510A after a 180 F post-cure.

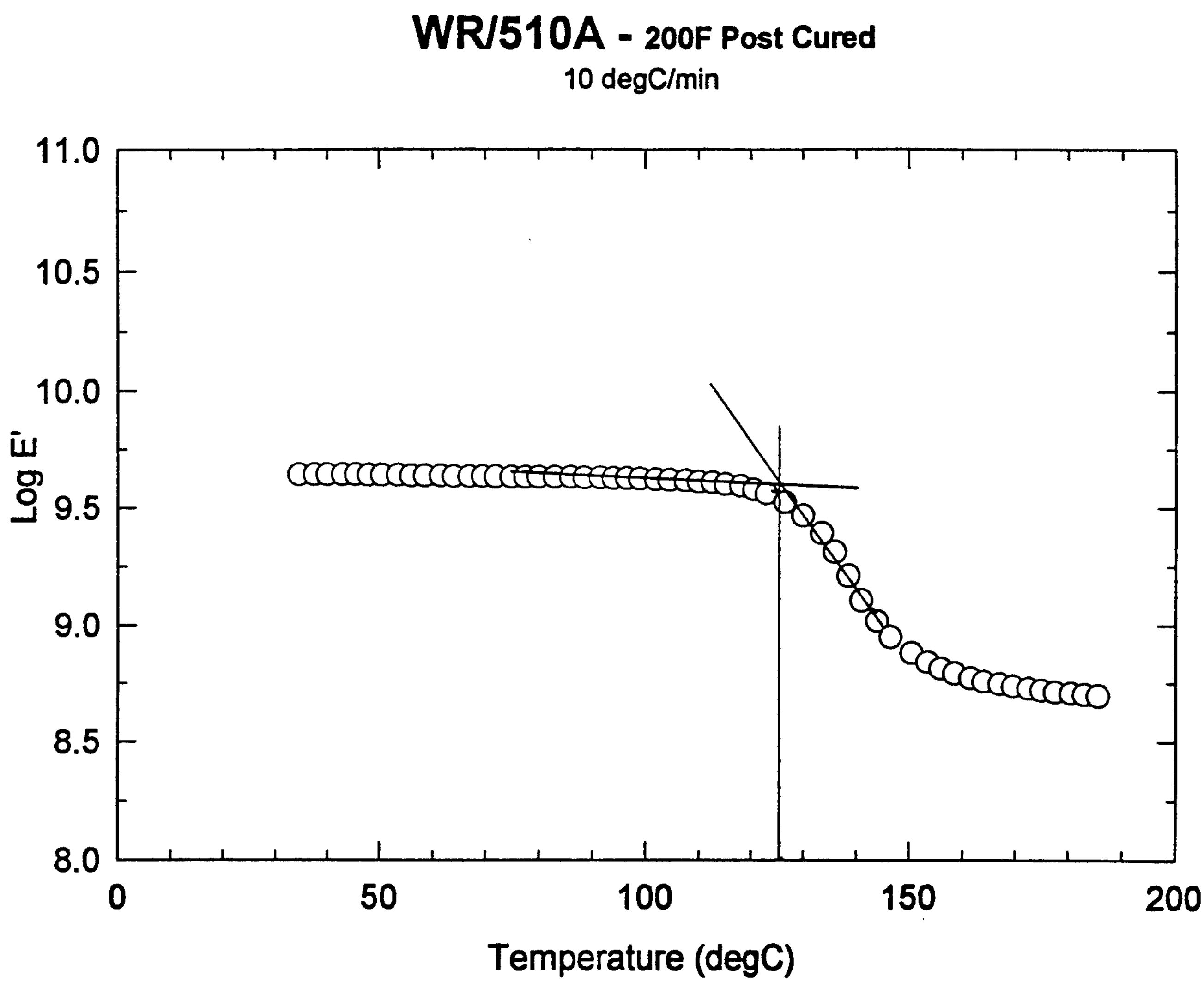

Figure 10. Modulus-temperature behavior of WR/510A after a 200 F post-cure.

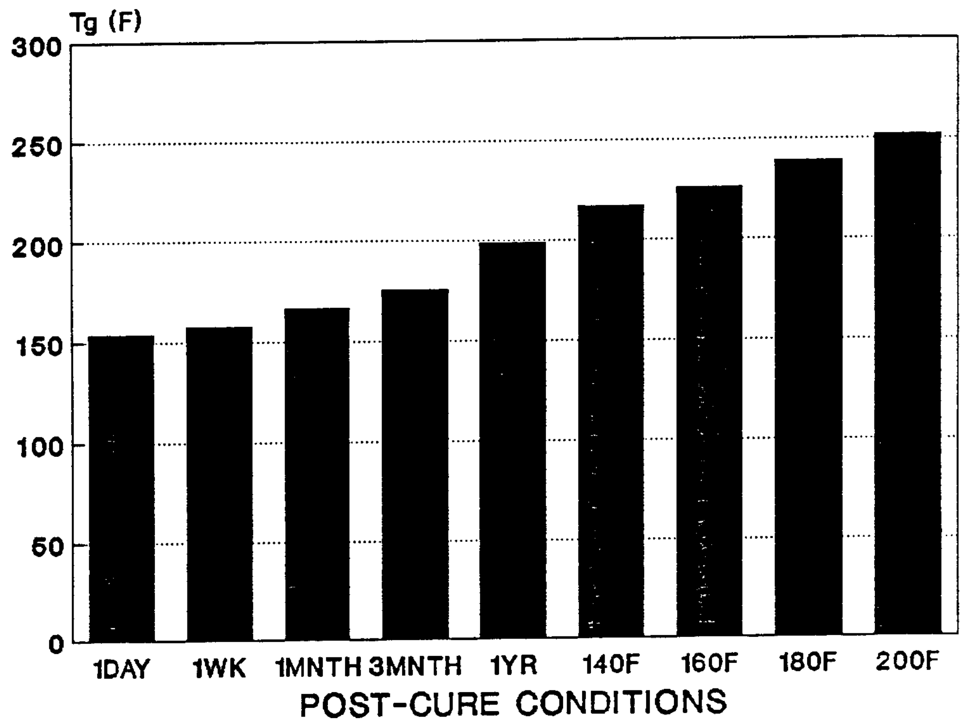

Figure 11. Tg of WR/510 A as a function of post-cure conditions.

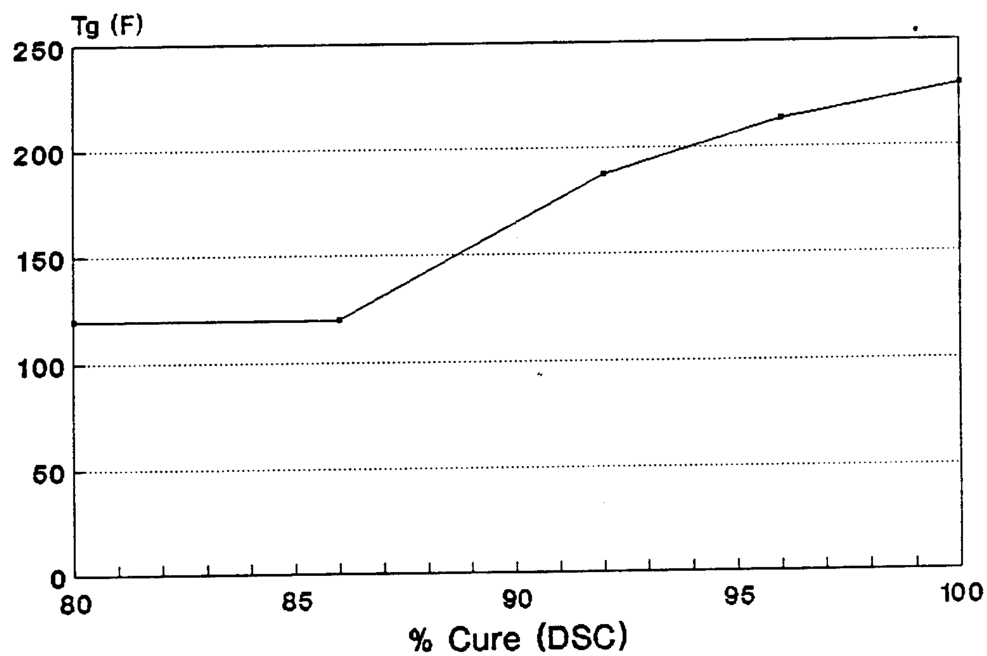

Figure 12. Tg as function of percent cure for Derakane 411 (data taken from reference 2).

APPENDIX. Raw Flexural Strength Data

Post-cure Temp;Time	thickness (inches)	width (inches)	load (lbs)	strength (ksi)
Ambient; 24 hours	.138	.505	72	50.5
	.135	.504	80	58.8
	.140	.507	73	49.6
	.138	.505	72	50.5
	.140	.503	75	51.3
MEAN				52.1
STD DEV				3.8
Ambient; 1 week	.134	.503	83	62.0
	.135	.503	82	60.4
	.136	.507	97	69.8
	.141	.508	90	63.1
MEAN				63.8
STD DEV				4.1
Ambient; 1 month	.141	.504	102	68.7
	.136	.499	92	65.0
	.138	.502	109	83.9
	.136	.503	103	74.7
MEAN				73.1
STD DEV				8.2
Ambient; 3 months	.136	.502	108	78.5
	.140	.503	105	71.9
	.135	.503	84	61.9
	.139	.504	99	68.6
MEAN				70.2
STD DEV				6.9
Ambient; 6 months	.135	.503	122	89.8
	.144	.507	85	54.5
	.135	.502	107	78.9
	.132	.505	115	88.2
MEAN				77.8
STD DEV				16.3
140 °F; 8 hours	.138	.501	113	79.9
	.134	.501	102	76.5
	.139	.501	114	79.5
	.139	.503	112	77.8
MEAN				78.4
STD DEV				1.6
160 °F; 4 hours	.138	.505	135	94.7
	.138	.503	131	92.3
	.140	.504	120	82.0
	.135	.505	123	90.2
MEAN				89.8
STD DEV				5.5

APPENDIX. Raw Flexural Strength Data, Cont.

Post-cure Temp;Time	thickness (inches)	width (inches)	load (lbs)	strength (ksi)
180 °F; 4 hours	.135	.504	91	66.9
	.134	.502	99	74.1
	.134	.500	90	67.7
	.139	.502	100	69.6
MEAN				69.6
STD DEV				3.2
200 °F; 4 hours	.140	.498	109	75.3
	.135	.505	89	65.3
	.137	.500	106	76.2
	.140	.499	104	71.8
MEAN				72.1
STD DEV				4.9

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